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THEORETICAL AND EXPERIMENTAL INVESTIGATION OF THE PHYSICS OF CRYSTALLINE SURFACES

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I. SUMMARY OF WORK

The major effort during the past year was concentrated on the following problems:

(1) The relation between structure of epitaxial films and surface and interfacial energies.

(2) Quantitative studies of the elastic and inelastic interactions of slow electrons with tungsten single crystal surfaces.

(3) The determination of nature and structure of surface layers with low energy electron diffraction.

(4) The relation between structure and electron emission properties of work function reducing layers on tungsten {110} planes.

(5) Momentum exchange of atoms on well defined single crystal surfaces.

(6) Theory of low energy electron scattering.

The work on problem (4) was mainly concerned with equipment construction, that on problems (1), (2), and (3) only in part. Therefore most of the results were obtained in problem areas (1), (2), and (3).

II. The relation between structure of epitaxial films and surface and interfacial energies (A. K. Green).

The study of the evolution of water from alkali halides has been completed (Second Quarterly Status Report (1 May-31 July 1967); J. Appl. Phys., May 1968). Results of these experiments are important for all epitaxy work using alkali halide substrates.

A good part of the effort in epitaxy was spent on the design and construction of equipment. The essential parts for the planned experiments, evaporation tank, multiple specimen holder, vacuum cleaving device, and Knudsen cell evaporator are operational. Present experiments using this system are aimed at determining the influence of ion impurities from the vapor source on the growth of gold on NaCl. Preliminary results are that screens maintained at low potentials (± 90 V) in the vapor path do not influence film growth.

The UHV grazing incidence electron diffraction unit was used during the past year in a continuing study of the growth of f.c.c. metals on alkali halides. The influence of Na on film growth was studied by depositing Na during and after Au deposition. Results show that Na deposited during Au deposition produces a {100}-oriented $NaAu_2$ single crystal film. Deposition of Na onto the (5x1) structure on a {100}-oriented Au film produces a one-third periodicity of the Au pattern in the ⟨110⟩ direction.

Experiments to determine the influence of impurities from the bulk on the epitaxy of f.c.c. metals have been started. The use of doped alkali halides for substrates will provide data on the influence of specific impurities on epitaxy. Results obtained using NaCl doped with 0.2% $CaCl_2$ are: nuclei on an air cleaved surface show a strong tendency to cluster and the decoration is considerably different than on an undoped crystal. The initial orientation is better on the vacuum-cleaved surface, as on undoped crystals, but is predominantly (111) in contrast to undoped crystals where it is (100). The orientation of moderately thick films is predominantly (111) on both air- and vacuum-cleaved surfaces.

III. Quantitative studies of the elastic and inelastic interactions of slow electrons with tungsten single crystal surfaces (J. O. Porteus).

Modification of the vacuum system and testing of beam-tracking and voltage-scanning equipment was completed, thus permitting extensive measurements of elastic or inelastic electron beam intensities before serious sample contamination occurs. Intensity vs. voltage ("I(V)") curves were run on the zero and first order elastic beams from a clean W(110) surface in the primary voltage range 25-500 eV and at angles of incidence ranging from 8 to 20 degrees. Discrepancies observed in the data taken from different parts of the sample are tentatively attributed to nonuniform surface irregularities. The nonuniformity is believed to result largely from different grains within the crystal, which have slightly different orientation and thus respond differently to the sample preparation procedure. In an effort to avoid this difficulty a Mo(110) sample was prepared from a crystal showing no evidence of grain boundaries. However, because of lack of success in producing an acceptably clean surface in this case, based on the observed and currently accepted LEED patterns, further work on Mo(110) will be deferred until more extensive sample-cleaning studies have been made with additional monitoring methods. Meanwhile, a second W(110) sample is under study, this from a crystal showing evidence of fewer grains than the first. Although some discrepancies are still present in the I(V) data, these are less pronounced than with the original specimen. In addition to rechecking the elastic diffraction with this W(110) sample, measurements of the energy spectra of inelastically scattered electrons as a function of emergence angle and primary voltage are also being made. At present attention is principally focussed on electrons which may be involved in a two-step process of energy loss to plasmons, followed by diffraction. Inelastic intensity maxima possibly attributable to this process have been observed at well-defined primary voltages and emergence angles. Systematic investigation of the occurrence of these inelastic beams in relation to that of diffracted elastic beams of equivalent secondary energy are now in progress. In addition, a computer program for differentiating and improving the resolution of measured electron energy-loss spectra has been substantially completed. Hopefully, this will be useful in investigating observed shifts of energy-loss peaks with emergence angle.

IV. The determination of nature and structure of surface layers with low energy electron diffraction (E. Bauer).

The low energy electron diffraction (LEED) studies during the past year can be divided up as follows: (1) A study of the surface structure of Ag{100}, Au{100} and Pt{100} surfaces and of the interaction layers formed in the presence of alkalis. (2) A study of the surface structure of the Si{111} surface and of the interaction products with evaporated Fe and Ni. (3) A study of the adsorption of CO and O_2 on W. During the second half of the report year Auger electron spectroscopy was added to the LEED system which proved extremely useful for the characterization of the surface. The existing Varian quadrupole was replaced by an Ultek quadrupole with mass range up to mass 500 which allowed monitoring of materials such as Au and $W(CO)_6$.

(1) The Au{100} and Pt{100} surfaces form the by now well-known and highly controversial "5x1" structure. As the nature of this structure plays an important role in an epitaxy model proposed by us (E. Bauer and A. K. Green, Second Quarterly Report, August 1966), it was studied in detail. It was found that the "5x1" structure could be enhanced by Na or K deposition onto Au and Pt, but that it could not be produced on the Ag{100} surface. In addition to the "5x1" structure, several other structures are produced with varying alkali content. Those with lowest alkali content (as determined by the amount of deposited alkali, by desorption experiments, and by Auger spectroscopy) are related to the "5x1" structure. If the "5x1" structure is interpreted by double scattering between a hexagonal surface layer and the substrate, these additional structures with low alkali content are also hexagonal layers with the same lattice constant but in a different azimuthal orientation with respect to the substrate. By proper heat treatment they can be partially interconverted; heating in oxygen suppresses this interconversion and stabilizes the "5x1" structure. In the case of Pt where the main K Auger peak does not coincide with a Pt Auger peak, a weak K Auger peak is observed on a surface with "5x1" structure and a stronger one on a surface which shows one of the structures which can be converted into the "5x1" structure. The tentative interpretation is as follows: All the structures which can be interconverted are due to very thin $NaAu_2$ (KAu_2), $NaPt_2$ (KPt_2) surface layers with their {111} plane parallel to the Au, Pt{100} surface. The azimuthal orientations of these layers depend upon their alkali content. The "5x1" has the lowest alkali content. This interpretation is in contradiction with the presently most widely accepted interpretation according to which the "5x1" structure is a feature of the clean surface. Some additional experiments will be done during the next report year before publication of our data.

(2) The "clean" annealed Si{111} surface has been found in many laboratories to have one or several of the following structures: Si{111}-7, Si{111}-$\sqrt{19}$, and Si{111}-5. Several models have been proposed for these structures, involving only Si atoms. We have found by Auger analysis that surfaces with the mentioned structures are not clean but contain Fe, Ni, and several unidentified impurities respectively. The LEED patterns are compatible with very thin Fe_5Si_3 and Ni_2Si surface layers for the first two structures (see encl. 1). The third structure has not been identified to date.

Deposition of Fe and Ni with subsequent heat treatment supports the impurity interpretation of the "clean" surface structures. More work will be done, especially reaction studies with NH_3 and PH_3 to confirm the interpretation.

(3) The "reactive" adsorption of CO on W resulting in a very thin $W(CO)_6$ surface layer, which was proposed previously (Annual Report, 1966/67, paragraph IV3) to explain the LEED pattern and desorption spectrum of CO adsorbed on the W{110} plane, was studied for CO on the W{211} plane. The LEED pattern was simpler than on the {110} plane, but was also compatible with a $W(CO)_6$ layer. The desorption spectrum similarly indicated several CO groups with differing bond strength to the substrate as it was found for the {110} surface, again in agreement with the $W(CO)_6$ adsorption layer model. More experiments still have to be done, especially with better single crystals, to strengthen the arguments for this model which is in contradiction to the presently accepted views of chemisorption of CO. (According to these views the CO groups which differ in the bond strength to the substrate are adsorbed on different crystal planes.)

V. The relation between structure and electron emission properties of work function reducing layers on W{110} planes (G. Turner).

During this report year, effort was concentrated in two main areas. First, the investigation of the W{110}-BaO system and second, the development of hardware and components necessary to modify the ultrahigh vacuum electron microscope (UHVEM) to a bent-beam system, i.e. separation of the incident and imaginary beams.

A preliminary study (see Third Quarterly Status Report, 1967) of the contamination rate of clean W{110} and the W{110}-BaO system under ultrahigh vacuum conditions, indicated a need to know more about the influence of the contaminant on the surface structure before any quantitative conclusions could be reached. This additional information can be obtained by LEED and LEEM and would be available in the UHVEM using the bent-beam mode of operation. This modification was therefore initiated during the last quarter of this report period and the mechanical phase of the change-over completed.

In the second part of the effort, a source for a high luminosity electron gun was studied using W{100}-Zr coated field emitter in a glass field emission tube mounted on a Vac-Ion pumped system. The principle results were: (1) the enhanced emission of the system is a thick film effect and cannot be explained by the dipole layer theory, (2) a decrease in emission with time is always observed and is believed due to ion bombardment, and (3) the tip can be reactivated many times by simple reheating. The same field emission tube was subsequently mounted on the diffusion pumped UHVEM system to compare the effect of the different pumping systems on emitter activation and life. No essential differences were found. It was confirmed that oxygen must be present during the deposition of the Zr for an active electron source to be formed.

A quadrupole magnetic lens was designed and built. It will be used to compensate for the astigmatism associated with the deflection field. A preliminary investigation of the imaging properties of the deflection and correction electron optics has been started.

VI. Momentum exchange of atoms on well defined single crystal surfaces (W. Faith and E. Bauer)

Work on this problem during this report year was mainly concerned with systems modification to obtain trouble-free operation and a better signal-to-background ratio for the molecular beam. The pumping system was completely rebuilt to include a 6" NRC diffusion pump, liquid nitrogen baffle, and bakeable 4" valve. The molecular beam source was modified to allow modulation of the beam and lock-in-detection of the scattered beam. Final assembly and testing of these modifications will be done early in the next report year.

VII. Theory of low energy electron scattering (E. Bauer).

The efforts were concentrated on numerical calculations of LEED intensities from W{110} and Ni{110} surfaces. The results indicated the necessity for an iteration process to determine self-consistently the attenuation of the incident and diffracted waves by primary extinction. Efforts to obtain sufficiently rapid convergence of this iteration process were not successful. This lead to temporary cessation of the calculations because of the excessive computing times required. Calculations will be resumed when experience with other approximation methods exists.

VIII. Publications

1. "Multiple Scattering Versus Superstructures in Low Energy Electron Diffraction," by E. Bauer, Surface Sci. 7, 351 (1967).

2. "Linear Unfolding Methods and Optimization for X-ray and Similar Spectra," by J. O. Porteus, J. Appl. Phys. 39, 163 (1968).

3. "Evolution of Water from Alkali Halide Single Crystals," by A. K. Green and E. Bauer, J. Appl. Phys., to be published.

4. "On the Nature of Annealed Semiconductor Surfaces," by E. Bauer, Phys. Letters, to be published.

Invited papers

1. "Vapor Growth," by E. Bauer, Annual Meeting American Crystallographic Association, Minneapolis, August 1967.

2. "A Simple Theory of LEED," by E. Bauer and H. N. Browne, LEED Seminar, Brooklyn Polytechnic Institute, September 1967.